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Thermal migration of deuterium implanted in graphite: Influence of free surface proximity and structure

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ABSTRACT

This paper is a contribution to the study of the behavior of activation products produced in irradiated nuclear graphite, graphite being the moderator of the first French generation of CO_2 cooled nuclear fission reactors. This paper is focused on the thermal release of Tritium, a major contributor to the initial activity, taking into account the role of the free surfaces (open pores and graphite surface). Two kinds of graphite were compared. On one hand, Highly Oriented Pyrolitic Graphite (HOPG), a model well graphitized graphite, and on the other hand, SLA2, a porous less graphitized nuclear graphite. Deuterium ion implantation at three different energies 70, 200 and 390 keV allows simulating the presence of Tritium at three different depths, corresponding respectively to projected ranges R_p of 0.75, 1.7 and 3.2 μm. The D isotopic tracing is performed thanks to the $D(^3He,p)^4He$ nuclear reaction. The graphite structure is studied by Raman microspectrometry. Thermal annealing is performed in the temperature range 200–1200 °C up to 300 h annealing time. As observed in a previous study, the results show that the D release occurs according to three kinetic regimes: a rapid permeation through open pores, a transient regime corresponding to detrapping and diffusion of D located at low energy sites correlated to the edges of crystallites and finally a saturation regime attributed to detrapping of interstitial D located at high energy sites inside the crystallites. Below 600 °C, D release is negligible whatever the implantation depth and the graphite type. The present paper clearly puts forward that above 600 °C, the D release decreases at deeper implantation depths and strongly depends on the graphite structure. In HOPG where high energy sites are more abundant, the D release is less dependent on the surface proximity compared to SLA2. In SLA2, in which the low energy sites prevail, the D release curves are clearly shifted towards lower temperatures when D is located close to free surfaces. Extrapolating our data to Tritium mobility in irradiated graphite, we show that thermal selective extraction of T would be all the more so efficient as the graphite structure is more disordered, which means in the most irradiated and damaged graphite zones in the reactor.

1. Introduction

Graphite has been used as neutron moderator in many types of nuclear reactors due to its ability to slow down fast neutrons without capturing them. Whatever the reactor design, the irradiated graphite waste management has to be faced sooner or later regarding the production of long lived radioactive species or radionuclides that might be dose-determining for disposal such as ^{14}C, ^{36}Cl or ^3H. Thus, all over the world, around 250,000 tons of irradiated graphite have been produced through commercial and military nuclear power operation. Many of these reactors are now being decommissioned. Whatever the management options, a particular attention should be paid to Tritium. This radionuclide that was mainly produced through thermal neutron activation $^6Li(n_{th},\alpha)^3H$ of ^6Li impurities [1], has a short life time (around 12 years) but it is a major contributor to the initial radioactive dose [2]. In particular, T release might impact safety of the dismantling operation stage as well as the radioactive waste package management at the operational stages of disposal. Indeed, according to its location and speciation in the irradiated graphite waste, it might be potentially released through isotopic exchange with water or

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water vapor. Thus, in order to anticipate eventual T release, its radioactive inventory, location and speciation in the irradiated graphite should be previously assessed and its behavior during dismantling and waste management foreseen.

The protocol used in this work is based on the use of D implanted graphite samples in order to simulate the presence of T, displaced from its original structural site through recoil during reactor operation. NRA (Nuclear Reaction Analysis) is particularly well adapted to the analysis of D. The implanted D profiles are analyzed using the $D(^3He,p)^4He$ nuclear reaction. First results on the effects of temperature on the behavior of D in nuclear graphite have already been reported in previous papers [3,4]. The aim was to elucidate the behavior of T during reactor operation and to explore options of thermal decontamination in inert gas or oxidizing conditions. The results show that the D release is strongly correlated to proximity of the free surfaces and also to the nature and relative abundance of the different D trapping sites. Thus, higher temperatures are necessary to detrap D located at high energy sites inside the crystallites compared to D located at the coke grain edges or in the porous binder.

It is important to remind that nuclear graphite has a polycrystalline structure and contains micrometer sized coke grains that are blended with coal tar pitch acting as a binder. The grains are formed by several more or less oriented crystallites with a size of a few hundreds nm and each crystallite is formed by a tri-periodic stacking of graphene planes. The structural organization and the graphitization level of nuclear graphite are thus strongly heterogeneous at different scales [5,6].Therefore, in order to get more insight into the D release mechanisms, we decided to investigate also the role of graphite structure using Raman microspectrometry. For this purpose, two kinds of graphite have been considered: (i) Virgin nuclear graphite provided by EDF (*Electricité De France*) with an average porosity of 32%; (ii) Highly Ordered Pyrolytic Graphite (HOPG) Grade SPI-1graphite whose micrometer sized crystallites are all oriented parallel to the HOPG platelet, giving it a perfect lamellar structure; this HOPG is highly crystalline and not porous. Then, in order to study the role of surface proximity on the D release, we implanted both kinds of graphite samples respectively at three different implantation depths.

2. Experimental

2.1. Sample preparation and deuterium ion implantation

The virgin nuclear graphite is issued from the UNGG (*Uranium Naturel-Graphite-Gaz*) CO_2 cooled reactor Saint-Laurent A2 (EDF, SLA2, St-Laurent-des-Eaux, France), currently under dismantling. The samples are cut to a size of about $9 \times 5 \times 4\ mm^3$ with a diamond saw and one face is polished down to the micrometer with diamond paste. HOPG is obtained from SPI Supplies (West Chester, US) through Neyco SA (Paris, France). We received the HOPG samples as 1 mm thick $10 \times 10\ mm^2$ plates. The plates are cut with a diamond saw into approximately $10 \times 5 \times 1\ mm^3$ plates. Both nuclear graphite and HOPG samples were annealed at 1000 °C–1200 °C for 8 h either in high vacuum ($P \cong 10^{-7}$ mbar) in order to desorb most of the gaseous impurities and also in order to anneal at least partially the defects induced by polishing (for the nuclear graphite samples).

The graphite samples are implanted with D^+ ions at room temperature (RT) under vacuum either using the 400 kV ion implanter IMIO400 of the *Institut de Physique Nucléaire* of Lyon (IPNL, France) or the 200 kV ion implanter EATON 200MC of ICube laboratory of the University of Strasbourg, France or the 500 kV ion implanter KIIA of the University of Helsinki, Finland. Deuterium implantation was carried out at three different energies, 70, 200 and 390 keV. A density of 2.2 g cm^{-3} was taken for HOPG samples (density of perfect graphite) whereas for SLA2, we have assumed a density of 1.92 g cm^{-3} which will be discussed in the next section. Hence, the respective projected ranges (R_p) deduced from SRIM 2011 [7] are respectively of 0.75, 1.7 and 3.2 μm for SLA2 and 0.65, 1.45 and 2.8 for HOPG. Since the D implantation profiles were subsequently analyzed by NRA with a detection limit around 1 at.% in our experimental conditions, D^+ ions were implanted at a fluence of 5×10^{16} D^+ cm^{-2}. On the basis of SRIM calculation, the D concentrations at R_p are respectively of 3.4, 2.9 and 2.5 at.% and the number of displacements per atom (dpa) at the projected damage range (R_d), using the Kinchin–Pease calculation mode, are 0.3, 0.28 and 0.25 for both types of graphite. It can be noticed that the implanted D concentrations are higher than those of T produced in graphite moderator during UNGG reactor operation which range from some ppb to several tenths of ppm. In spite of the relatively high D^+ fluence, the maximum amount of displaced atoms generated by the implantation process in the graphite matrix remains quite low, around 0.3 dpa.

2.2. Analysis of the implanted deuterium

The D profiles were analyzed using the $D(^3He,p)^4He$ nuclear reaction with an incident ^3He beam. This reaction has already been used in particular in the context of studies devoted to fusion reactors [8–10].The analyses were carried out with a millimetric beam at the 4 MV Van de Graaff facility of IPNL. The reaction produces 13 MeV protons and 2 MeV $^4He^+$ particles. The incident beam was normal to the sample surface and only protons were detected at 155° using a 2000 μm thick Si surface barrier detector with a solid angle of 12 msr. A 23 μm thick Mylar® screen was placed in front of the detector to stop the emitted $^4He^+$ particles as well as the backscattered $^3He^+$ particles. Experimental details can be found in Refs. [3,4].

Depending on the increasing implantation depths, the D profiles were analyzed using increasing $^3He^+$energies of 900, 1150 and 1600 keV. These energy values allow adjusting the maximum of the $D(^3He,p)^4He$ reaction cross section σ_{NRA} located around 620 keV at a detection angle of 135° [11], as close as possible to the calculated D projected ranges. As mentioned previously, a density of 2.2 g cm^{-3} was assumed for HOPG due to its highly ordered state and its perfect lamellar structure whereas for the SLA2 samples, a lower density of 1.92 g cm^{-3} was chosen due to its porous structure. Fig. 1 represents the D distribution profiles for both graphite grades as a function of depth for the implantation energy of 390 keV. This figure shows the implantation profiles

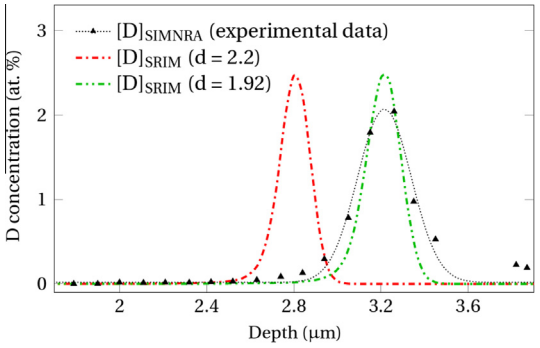

Fig. 1. D distribution profiles in graphite as a function of depth for an implantation energy of 390 keV: experimental (black triangles) and fitted SIMNRA profile (black dotted line) and SRIM calculated profiles for respective densities of 1.92 g cm^{-3} (green dashed dotted line) and 2.2 g cm^{-3} (red dashed dotted line). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)